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DESCRIPTION

FIELD EMISSION CATHODE AND FIELD EMISSION DISPLAY

The present invention is concerned with field emission electrodes and with field emission displays.

A great deal of research effort has been devoted in recent years to developing a display which can replace the conventional cathode ray tube (CRT). Shortcomings of the CRT include its weight and bulk, and also its requirement for relatively high input power. The CRT is also unsuited to use in large area displays eg. in stadia and in small displays for laptops, watches etc.

The liquid crystal display (LCD) provides an alternative which is not subject to some of the disadvantages of the CRT. It can be manufactured in flat panel format, and used both in miniature displays and in larger displays, eg. in wide format television sets. However, LCD displays suffer from disadvantages of their own, particularly with regard to display brightness.

A promising alternative to both LCDs and CRTs is the field emission display (FED). FEDs offer the prospect of flat panel displays which are superior to LCD screens in brightness, colour rendition, response time and operating temperature range.

In known FEDs, electrons are released from a cathode by field emission (rather than by thermionic emission, as in the CRT) and accelerated toward an anode which is maintained at a positive potential typically of several kV. The electrons

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impinge on the phosphor pixels which are thereby caused to luminesce, providing the display. To generate the field needed for release of electrons, a matrix of switchable row and column electrodes is typically provided, in addition to the anode, and in this way pixels can be individually addressed.

A particular problem has been found in providing a cathode which exhibits field emission at electric field strengths which can be provided in a practical display, without the need for unacceptably large power and voltage.

Known FEDs typically utilise cathodes having on their surface an array of microscopic pointed elements known as Spindt tips, formed of Mo or Si. The tips are very sharp - having radii of the order of 20nm - thereby providing large local electric fields to cause field emission. This is necessary because in the materials of such known cathodes the work function (the energy needed to release an electron from the cathode) is otherwise relatively high - of the order of 5eV. These known cathodes are not straightforward to manufacture and suffer from reliability problems due to erosion of the field tips.

An alternative approach which has been proposed is to provide a cathode lacking Spindt tips but formed of material having low (or even negative) electron affinity. Electrons may be released from such a material by relatively small electric fields.

There is in almost all such field emission systems the need to electrically condition the cathode before low threshold emission is possible. Diamond like carbon (DLC) films have given high emission, particularly when doped with

nitrogen. One such doped material has provided what is believed to be the lowest threshold reported at the priority date. The nature of the bonding is thought to be an important factor with diamond-like sp³ bonds being appropriate for producing the energy levels associated with a low electron affinity.

Current understanding of the main features of the emission processes is incomplete, but it is believed that the density of sp³ bonds and the presence of hydrogen are important. An alternative model is based on a dual process which involves electron heating in the DLC conduction band due to its internal electric field and emission over the relatively low surface potential barrier (electron affinity). Nitrogen acts as a donor fostering the formation of a high field depletion region. This high field region promotes transfer of electrons from substrate to film.

Although DLC film cathodes have hitherto been considered the most promising candidate, the results have not been sufficiently impressive for displays based on such materials to be considered an immediate replacement for the CRT and LCD.

A first object of the present invention is to provide an improved field emission cathode.

It is desired that such a cathode should exhibit field emission when subject to an electric field of a magnitude which can be created in a practical display.

It is additionally or alternatively desired that such a cathode should exhibit stable field emission properties.

It is additionally or alternatively desired that such a cathode should be capable

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of manufacture in suitable form for use in a field emission display.

In accordance with a first aspect of the present invention, there is provided a field emission cathode comprising conjugated polymer material forming a field emission surface.

The inventors have fortuitously (and most unexpectedly) discovered that polymer materials can be manufactured giving high electron emission. Polymer materials can be formed by known techniques into uniform cathodes, which may be large in area, and can be highly stable. Exclusion of oxygen is considered useful for the stability of the material.

Conjugated polymers typically have high density of free electrons. Most polymer films are p type with few free electrons; the substrate of the cathode can itself contribute electrons.

Such materials are known for other applications in electronics, which utilise semiconductor type properties of certain conjugated polymers. The usual applications proposed for conjugated polymers - eg. in light emitting structures, photocopiers, photodetectors and thin film transistors - do not require the material to have a low work function, and it is believed that this property of such materials has not hitherto been utilised. The present inventors have found that some such polymeric materials are capable of producing very high steady state field emission currents with the threshold field needed to initiate field emission being smaller than for any other so far reported.

It is especially preferred that the polymer material is a substituted

polythiophene, and polyalkylthiophenes are particularly suitable. Poly -3-octylthiophene is currently the preferred material.

The polymer material may take the form of a layer on a substrate. It is especially preferred that the polymer layer is formed as a film with thickness of the order of 5μm.

The polymer material is preferably spun from a liquid source or is evaporated in a vacuum onto a substrate, techniques which can produce a large area cathode. A light and economical cathode can be produced in this way.

It is preferable that the polymer material should have a low barrier to electrons of the substrate on which it is formed.

The polymer material may be doped with an electron donor material The electron donor may be nitrogen (known to reduce the barrier to electrons of the substrate of diamond-like carbon). In fact, un-doped polymers have relatively low number of electrons but transport electrons from the substrate very efficiently. This leaves a great deal of scope for improvement by doping.

The polymer material may have energy levels which trap electrons serving to concentrate the electric field. In this way, field emission is promoted. In a preferred structure, the polymer material forms a film on a substrate comprising microcrystalline silicon. The grain boundaries at the polysilicon surface trap large numbers of electrons as the surface becomes more n type, and so are able to concentrate the field at these points, promoting increased emission from the polymer film.

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It is believed that in the material samples which led to the inventors' initial discovery, voids observed on the material surface, believed to be due to solvent evaporation, serve to create large local electric fields at certain parts of the field emission surface and to promote field emission.

However, a great advantage of the use of polymer materials is that many of them can be shaped by use of a mould. The term "mould" as used throughout this document must be understood to include any type of process in which the polymer is shaped by contact with an appropriately formed tool which is then removed and "moulding" is to be correspondingly construed. By moulding the polymer 's emission surface can be shaped such as to promote field emission, eg. by forming tips thereon.

In accordance with a further aspect of the present invention, there is a field emission display having a cathode in accordance with the first aspect of the invention.

There are however other applications for the cathode.

At the low field strength which is sufficient to cause field emission from the cathode according to the present invention, emitted electrons may be insufficiently energetic to cause luminescence of a display screen. This problem is experienced when a phosphor screen is used.

Hence a preferred from of visual display device according to the present invention comprises a grid positioned with respect to the cathode such as to be capable of causing field emission therefrom, an acceleration anode positioned beyond

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the grid and a luminescent screen, wherein electrons are selectively emitted from the cathode under the influence of the grid and then accelerated onto the screen with sufficient energy to cause it to luminesce by the acceleration anode.

In accordance with a third aspect of the present invention, there is a method of fabricating a field emission cathode comprising forming a layer comprising conjugated polymer material on a substrate, the polymer material forming a field emission surface of the cathode.

The polymer material may be any of the polymer materials referred to above with respect to the first aspect of the invention.

Specific embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:-

Fig. 1 is a graph of normalised or average field emission current density (on a logarithmic scale of Acm^{-2} on the vertical axis) against applied voltage for a cathode embodying the present invention;

Fig. 2a is a graph of normalised field emission current density from a cathode according to the present invention in $A cm^{-2}$ and a logarithmic scale on the vertical axis against normalised applied electric field on the horizontal axis, measured in volts per μm. Results are shown for three anode-cathode spacings, the left-most line being for a spacing of 27μm, the middle line for 47μm and the right-most line for 130μm;

Fig. 2b is a graph of normalised field emission current density from a cathode according to the present invention in $A cm^{-2}$ and a logarithmic scale on the vertical

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axis against applied anode voltage on the horizontal axis. Results are shown for the three anode-cathode spacings mentioned above with reference to Fig. 2a;

Fig. 3 is a graph of field emission current from a cathode according to the present invention in μA on the vertical axis against time in hours on the horizontal axis;

Fig. 4 shows band diagrams for a cathode according to the present invention comprising a P3OT layer on a p-Si substrate when subject to no bias (Fig. 4a) and when subject to a biasing field from an Al anode (Fig. 4b);

Fig. 5 shows band diagrams for a cathode according to the present invention comprising a P3OT layer on a n-Si substrate when subject to no bias (Fig. 5a) and when subject to a biasing field from an Al anode (Fig. 5b);

Fig. 6 is a band diagram representing a model for the field emission of electrons into the vacuum from a cathode according to the present invention;

Fig. 7 represents a simple model of field emission from a cathode according to the invention;

Fig. 8 schematically illustrates energy levels in the region of a void of the surface of a cathode according to the present invention;

Fig. 9 is a graph of predicted field emission current (in a logarithmic scale as the vertical axis) against anode voltage on the horizontal axis assuming a simple one dimensional model for three different anode/cathode separations;

Fig. 10 illustrates a step in the process of moulding a polymer layer of a cathode according to the present invention, the cathode and mould being seen in cross

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section;

Fig. 11 illustrates in cross section a structure of a display device constructed in accordance with the present invention; and

Fig. 12 illustrates in cross section a further structure of a display device according to the present invention.

A first specific embodiment of the invention comprises a field emission cathode formed as a thick (5μm), spin-cast, nominally undoped polymer (regioregular poly-3-octylthiophene - P3OT) which is capable of high, stable electron emission. The observed threshold field (0.2MVcm-¹) is the lowest so far reported among carbon based materials.

P3OT can be synthesised in pellets by the technique reported in Chen, T-A,Wu,X-M & Rieke, R.D.: Regiocontrolled synthesis of poly (3-alkylthiophenes) medicated by Rieze inc: their characteristics and solid state properties, J.Am. Chem. Soc. 117,233-244 (1995). However during trials carried out by the inventors the material was purchased from a commercial source.

During trials, chloroform has been used as a solvent: dissolving 5mg of P3OT in 1ml of chloroform resulted in films of thickness 5μm.

In initial tests the solution was cast onto a pre-cleaned 1cm x 1cm highly doped n-Si substrate (resistivity 0.003-0.01Ω cm) in a clean non-vacuum atmosphere. The optical Tauc bandgap was determined, at room temperature, to be -1.75eV by ultraviolet-visible spectrophotometry (this bandgap is defined as the intercept of the gradient of a $(\alpha\ E)^{\frac{1}{2}}$ versus E plot with the E axis where α is the absorption

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coefficient and E the photon energy). In addition, a single broad absorption maximum was observed at ~ 2.38eV, which suggests that these "as synthesized" films are only slightly doped. Nuclear magnetic resonance measurements indicate a regular "head-tail" arrangement of the alkyl side chains (which can be thought of as a measure of how ordered the polymers are) of >90%. Such high regularity has only recently become available. It may not be essential for this application. Following casting the P3OT/n^{++}- Si devices were immediately placed in a vacuum of pressure ~10^{-7} torr to dry for 24 hours.

No special processes were introduced to eliminate the effects of light or air during preparation of the films. Hence in these initial trials they were invariably p type.

Field-emission experiments have been carried out using cathodes formed in the above manner in the flat plate configuration with an indium tin oxide coated glass anode. The separation between the anode and cathode was varied between 27μm and 130μm using glass-fibre spacers. The pressure in the vacuum was ~2 x 10^{-7} torr. As with many carbon based materials it was necessary initially to ramp the anode voltage to a high level to achieve field emission - ie. to condition the film. Fig. 1 shows typical current-voltage (I-V) characteristics. Two regions are clearly identified (called here 1 and 2). Regions 1a and 1b represent the emission before conditioning and region 2 is after conditioning. A highly stable and reproducible current level was maintained after conditioning. The conditioning field was always below 10Vμm^{-1} in order to avoid any influence of vacuum breakdown phenomena,

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which can occur at fields above $15V\mu m^{-1}$ at the pressure used.

The results were found to be repeatable with or without the spacer being in contact with the ITO anode. Raising the pressure caused the emission current measured at the anode to fall to zero. The emission current was found to scale with the area of the film rather than its perimeter, indicating that edge effects were not dominant.

The remarkable current density (J)- electric field (F) characteristics, with threshold field of only ~$0.2V \mu m^{-1}$ for a current density of $1\mu A$ cm^{-2}, are shown in Fig. 2a. Fig. 2b shows the J-F characteristics as a function of anode-cathode spacing. In addition a slope of 1.8 of the log I-log V plot indicates that a space-charge-limited current (SCLC) may be limiting the emission process. The measured anode voltage versus gap separation is shown in Fig. 2a inset and indicates a nonlinear relationship. This shows that surface and bulk charge properties may be important to the emission process.

The surface morphology of the film was examined by scanning electron microscopy (SEM) both before and after field emission. There was no apparent explosive destruction of the film, which can be associated with discharge current phenomena during field emission. The polymer films show void-like features on the surface, of density ~4 x 10 cm^{-2} and of sizes ranging from $0.40\mu m$ to a few micrometres.

The inventors also examined the stability of the emission current over time. The emission characteristic recorded over a 16 hour period of continuous emission

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is shown in Fig. 3. The initial current drops to 55% of its value in 2 hours, and thereafter remains stable. The sensitivity of the emission to a change in pressure was also examined: the emission current dropped to below 10pA when the pressure rose to 10^{-3} torr.

An explanation of the current understanding of the physics of certain exemplary embodiments of the present invention is given below, but it must be understood that the inventors do not thereby intend to limit themselves to any particular model or theory explaining the operation of the present invention.

The band diagram of Fig 4 for an aluminium anode predicts a very rapid rise of current which is observed with positive voltage on the aluminium. Space charge limited current kinks would be expected with a high density of donor-like traps in the bottom half of the P3OT energy gap. Al gives excellent Schottky barriers on p-Si, with high on/off ratios.

The band diagram for the n substrate (Fig. 5) also predicts high forward currents, this time due to electrons. Now there is significant distortion due to the effects of trapped electrons in acceptor-like traps in the top half of the band gap. Only a single trapping level is apparent, although a second one could be the cause of the saturation of the current at about 10^{-4} A. A second interpretation is considered less likely: a low density of states at the edge of the conduction band could, in principle, explain the dominance trapping and hence the presence of such distinct space charge limited effects.

The inventors conclude that the n-Si barrier is a reasonably efficient injector

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of electrons, that the effective lifetime of electrons in the polymer is, for minority

carriers, surprisingly large. The density of traps in the top half of the polymer energy

gap is significantly higher than in the lower half.

A further condition must be met for efficient field emission: there must be an

efficient mechanism for injection of electrons into the vacuum. The electron affinity

of polymers is low but positive. There is, therefore, a barrier to electrons at the

surface of the polymer. Electrons concentrate at this barrier, and most become

trapped in the top half of the energy gap, close to the surface. There will, therefore,

be significant curvature of the conduction band, with the Fermi level near to the

conduction band edge. This promotes electron emission via tunnelling across the

barrier (Fig. 6). Some of the electrons may travel ballistically across the narrow

surface space charge region where they encounter a smaller tunnelling distance.

Further down the conduction band where the concentration of free electrons is higher

the tunnel distance is lower. Fig. 7 shows the proposed model in its simplest form.

The electron density falls with distance from the silicon cathode, whilst the field

increases to maintain nE and therefore the current density constant. Standard analysis

of space charge limited currents in thin films gives.

$$Jx_f = \frac{(\Theta \mu \epsilon)\,(E_1{}^2 - E_2{}^2)}{2}$$

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where x_f is the film thickness, Θ is the ratio of the free to total electron concentration in the film, μ is the free electron mobility, $\varepsilon = \varepsilon_0 \varepsilon_r$ where ε_r is the relative permittivity of the polymer and ε_0 is the permittivity of free space. E_1, E_2 and E_{vac} are various field strengths defined in Fig. 5.

The field within the surface of the polymer and the field in the vacuum are related by:

$$\varepsilon E_2 = \alpha\, \varepsilon_0 E_{vac}$$

where α is the field intensification multiplier just outside the polymer surface.

As mentioned above, there is evidence from AFM and SFM pictures that voids exist in the surface of films prepared in the way described above. It is proposed that these voids are the source of the field intensification and that the electron current that flows has two components, one from the space charge limited behaviour described above and a second due to free space charge within the void itself. Such a current would also be space charge limited obeying Child's Law. Both of these forms of space charge limited current have the form $J \alpha\, V^n$ where $n=1.5$ in the case of vacuum (Child's Law) and $n=2$ with solids. The rim of the void is found to have a lip, shown schematically in Fig.8, together with the regions where $n=1.5$ and $n=2$. The lip will act as an effective intensifier of the field.

Because the vacuum gap is much larger than the film thickness the two forms of current must mix in this region and space charge in the vacuum due to Child's Law, in the region above the lips, will regulate the current from the $n=2$ region. Similarly abrupt changes of potential will not be possible between the lips and the

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adjacent space in the void - which is of the order of 1 μm in diameter or less. This
will regulate current form the void. These effects are not amenable to 1D analysis,
so we make a simplifying assumption that the two current densities are equal, as are,
approximately, the two areas of emission. The resulting current voltage plots are
shown in Fig. 9 for the three vacuum gaps used in the field emission experiment.
Although the plots accurately predict the slope of 1.8 for all three cases, as well as
for a range from 10V to 1KV (not shown), there is a discrepancy in the thickness
dependence.

Strictly speaking one would expect the simple analysis provided here to only
apply for vacuum gaps comparable in size to the thickness of the polymer film.
Extension to greater gap size is the subject of 2D modelling.

The inventors have speculated that the voids in the polymer film may be
created by solvent evaporation during the manufacturing process. In working
displays an alternative method of creating the necessary morphology is considered
desirable and to this end the polymer film may be shaped against a mould. In such
a process, the polymer material may be cast or centrifugally spun and thereby
distributed over the substrate. A female mould, seen at 100 in Fig. 10, is then pressed
against the upper surface of the polymer 102. In Fig. 10, the substrate is seen at 104.

Polymers can be well suited to moulding processes.

In the illustrated embodiment, the mould is shaped to form in the polymer a
number of emission tips 106.

Display devices embodying the present invention are illustrated in Figs. 11

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and 12.

In the simplified FED device structure illustrated in Fig. 11, the field emission cathode is a flat film 2 of polymer material disposed on a conducting substrate 3 maintained at low electrical potential. An anode 4 is provided in front of the cathode, and bears pixels 5 of a material which emits light when struck by energetic electrodes, to produce the display. The anode may consist of a light emitting phosphor on glass. Between the anode and the cathode is a grid 6 which can be selectively positively charged. The space 7 between the anode and the cathode is a vacuum.

In operation, selected regions of the grid 6 are charged positively (relative to the cathode) producing the field necessary for field emission of electrons from corresponding regions of the cathode. These electrons are accelerated through the grid by the electric field due to the anode 4, and strike the anode causing it to emit light in selected regions of the screen.

A more detailed illustration of a suitable device structure is given in Fig. 12. Here the cathode is formed by a shaped polymer layer 52 on a substrate 54 which may be of glass. Spacers 56 separate the cathode from a conducting grid 58, penetrated by apertures 60 through which emitted electrons can reach a screen forming the anode and comprising a luminescent phosphor anode 62 on a glass substrate 64. Here it is the grid 58 which modulates the field emission (being positively charged relative to the cathode to the low voltage needed to produce field emission with the type of cathode described herein). The anode 62 is maintained at

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a higher voltage to accelerate the electrons sufficiently to cause the phosphor to

luminesce with a required intensity.